The Delivery of Chromophoric Dissolved Organic Matter to the Sea

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LONG-TERM GOAL

The long-term goal of this research is to better understand the biogeochemical cycling of dissolved organic matter (DOM) in coastal waters. Of particular interest is the fate of terrigenous and dissolved organic matter in coastal marine systems and its affects on ocean color.

OBJECTIVES

1.) *Determine high resolution spatial and temporal variability of chromophoric dissolved organic matter (CDOM) in coastal regions*.

By applying recent advances in *in situ* measurement and real-time sampling, the differentiation of sources, synoptic mapping of distributions, and predictions of transformations of CDOM will become possible.

2.) *Determine the reactivity of DOM in estuaries*

By examining sources and sinks of colored and non-colored DOM along salinity gradients, estimates of water mass residence times can be converted to average reactivities for the various sources of DOM

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14. ABSTRACT
The long-term goal of this research is to better understand the biogeochemical cycling of dissolved organic matter (DOM) in coastal waters. Of particular interest is the fate of terrigenous and dissolved organic matter in coastal marine systems and its affects on ocean color.

15. SUBJECT TERMS

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in coastal waters. Only through high resolution, highly sensitive measurements may the different reactivities of several sources of CDOM be determined simultaneously.

3.) *Relate the molecular level structure of DOM to the optical properties of CDOM.*

Detailed molecular level characterization of DOM isolates by ^{1}H NMR, Pyrolysis GCMS, and lignin analysis will supply valuable structural information to augment optical measurements of CDOM. In order to reliably predict the important photochemical, biological, and chemical processes governing CDOM, and hence its reactivity, the link between structure and optical properties must be defined.

4.) *To address the long-standing question: How much seawater DOM is derived from terrigenous sources?*

Differentiation of sources with both optical and chemical characterization techniques will allow an estimate of dissolved organic carbon (DOC) flux out of different estuaries into the open ocean.

APPROACH

New undulating, towed sensor systems (undulating 3-50 m—ECOShuttle; tow-yo 0-3 m--MiniShuttle) designed specifically for optical measurements of CDOM now allow high spatial resolution CDOM measurements and have been deployed in Boston Harbor, Delaware Bay/Chesapeake Bay, San Diego Bay, San Francisco Bay, Gulf of Mexico, and several northeast salt marsh estuaries. Discrete seawater samples have been taken (via submersible pump incorporated into the towed systems) in order to validate *in situ* measurements while large volume samples were taken to characterize the various sources of CDOM. Optical measurements include absorption spectra, fluorescence excitation-emission spectra, and time-resolved fluorescence spectra. Further analyses include high-temperature combustion dissolved organic carbon, ^{13}C and ^{14}C concentrations in various organic pools, chlorophyll-a, and elemental analysis. CDOM characterization will rely on ^{1}H-NMR and direct temperature mass spectrometry (DTMS) of the high molecular weight fraction of DOM isolated and concentrated by ultrafiltration (>1000 NMW). This project is an interdisciplinary effort combining physics (Gardner), organic geochemistry (Chen) and isotope geochemistry (Wang).

WORK COMPLETED

Two studies of the Mississippi River Plume in the Gulf of Mexico in June, 2000 and April, 2001 were conducted. In June, 2000, a very low flow period, over 1000 miles were covered in the area both to the east and to the west of the Birdfoot Region of the Mississippi River Plume yielding over 10 million *in situ* measurements of CDOM along with other relevant oceanic parameters. In April, 2001, a high flow period, over 900 miles were covered mostly outside the southwest pass region to the west (Figure 1). During this second cruise, 3 drifters were placed at the mouth of the river (Hitchcock) and followed for approximately 60 hours. Both cruises were interdisciplinary involving 16 scientists from 7 institutions investigating physical, optical, microbial, photochemical, isotopic, zooplanktonic, and trace metal aspects of CDOM associated with the Mississippi and Atchafalaya Rivers entering the Gulf of Mexico.

In addition, seasonal studies have been carried out in the Neponset River estuary (Boston Harbor) and Plum Island estuary (Plum Island Ecosystems Long Term Ecological Research site, north of Boston).

Both areas are lined by tidal salt marshes which produce CDOM in the mid-estuary. CDOM production within the salt marsh (wells placed in a transect from estuary into the salt marsh) as well as high resolution transects with the Mini-Shuttle were carried out from October, 2000 to September, 2001.

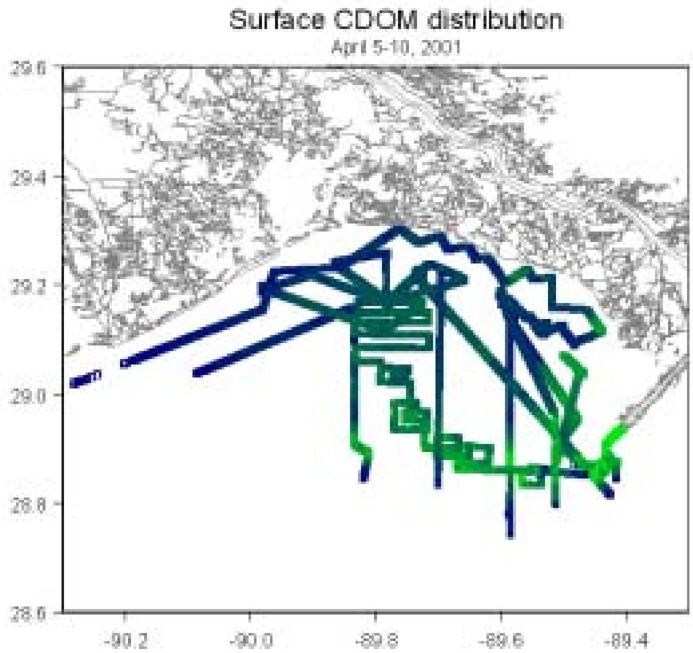

Figure 1. Surface CDOM distribution measured on a pumped flow from approximately 1 meter depth. The Mississippi River plume can be seen traveling (and being diluted) to the northwest from Southwest Pass where three drifters were released. Cruise tracks were designed to follow the drifters, provide large areal coverage, and investigate the nearshore region where there was a clearly observable delineation between the Mississippi River plume and the nearshore waters.

RESULTS

1.) CDOM fluorescence is not simply driven by conservative mixing of a freshwater endmember with seawater. In many cases, major sources of CDOM occur within estuaries (salt marsh contributions in San Francisco Bay, Neponset River, and Plum Island Estuary; benthic fluxes in San Diego Bay) and even on continental shelf systems (phytoplankton production in the Middle Atlantic Bight).

2.) Fluorescence-salinity relationships change from estuary to estuary and with season suggesting that watershed characteristics affect CDOM concentrations and distributions. It appears that high flow estuaries in general have lower freshwater CDOM endmember concentrations than low flow estuaries. Wetlands appear to be significant sources of CDOM as can be seen in the Atchafalaya River endmembers being significantly higher than those in the Mississippi River, with its highly engineered river banks (Figure 2). It also appears that salt marshes produce significant amounts of CDOM in the summer and late fall with little or no input in the spring before the major *Spartina spp* production and decomposition.

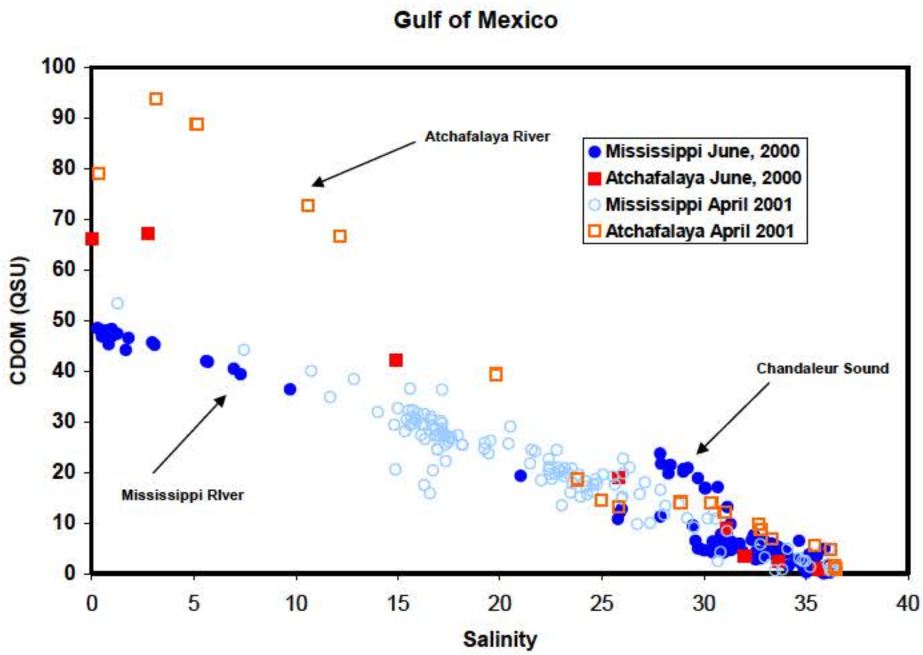

Figure 2. Salinity vs CDOM fluorescence for the June 2000 and April 2001 Mississippi River cruises. Mississippi River CDOM shows little seasonal variation. In contrast, the Atchafalaya River, which splits from the Mississippi River above New Orleans shows a higher freshwater endmember than the Mississippi, and is also higher during the high flow period (April 2001).

3.) A biological source of CDOM was evident during the highly stratified and stable period in June 2000. This biological source was not clearly observable during the higher flow period in April, 2001. The optical properties of this subsurface CDOM were similar to riverine CDOM, however the microbial characteristics were distinct (Moran and Zepp, personal communication).

4.) Evidence for photochemical bleaching in water masses further from the Mississippi River mouth was observed. We are still examining data associated with the drifters to try to determine rates of photobleaching.

5.) Deployments of the Mini-Shuttle, a micro-CTD and CDOM fluorometer mounted on a small depressor wing, show microstructure in CDOM distributions in estuaries. Over small vertical scales of <1 meter, variations in salinity from 10 to 25 (Figure 3) and associated CDOM concentrations were apparent suggesting care must be taken in interpreting discrete samples taken within the upper 3 meters of the ocean as well as remote ocean color measurements that measure the upper few meters of the ocean.

IMPACT/APPLICATIONS

High resolution optical measurements allow a much better understanding of complex coastal processes. With a significant groundtruthing effort, this research yields a new, powerful technique for examining episodic and small-scale events and features in coastal waters. Our data show variations in CDOM intensity over very small scales (10s of meters horizontally, centimeters vertically) while CDOM composition shifts regionally (10s of kilometers or with watershed). Further examination of the discrete large volume samples should yield valuable information on the reactivity of the CDOM in estuaries as well as the relationship between optical measurements and CDOM composition.

Further, it appears that freshwater discharge and land use are master variables controlling the concentration of terrestrial CDOM that enters and passes through estuaries before entering coastal waters. If these relationships hold up, it may be possible to predict the flux of CDOM into coastal regions worldwide.

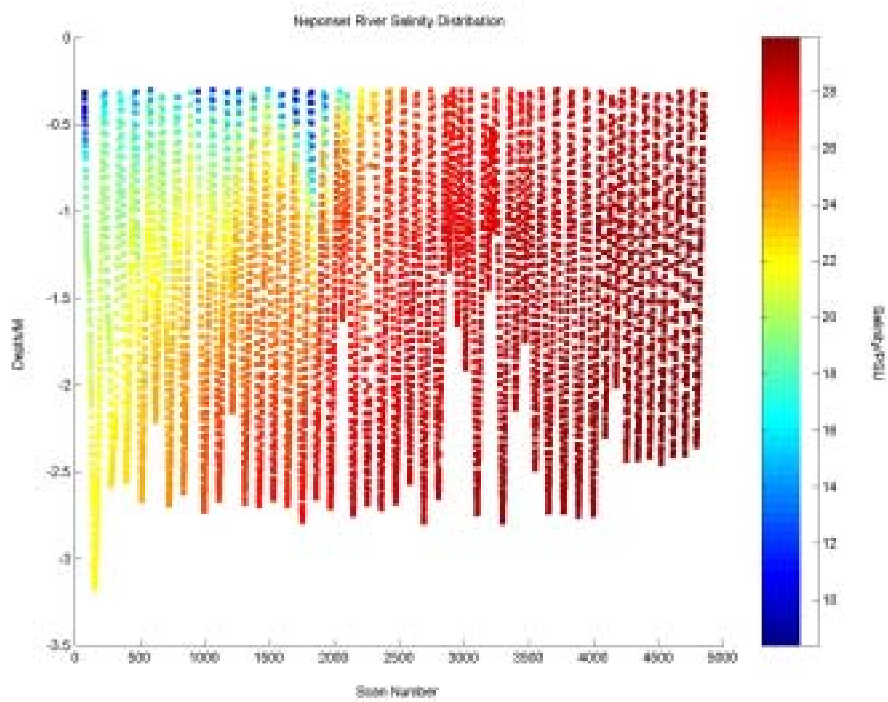

Figure 3. Salinity with depth vs scan number (time) in the Neponset River estuary (total distance is about 3 miles). The intrusion of the salt wedge from the right to the left is clearly seen. In addition, a periodic oscillation of the halocline is seen in the mid-estuary suggestive of internal waves controlling the two-dimensional distribution of salinity (and associated CDOM) in the estuary. A similar two-dimensional distribution was seen at the bottom of the Mississippi River plume in the Gulf of Mexico.

TRANSITIONS

The results of our multi-PI cruises in the Gulf of Mexico a well as the west Florida Shelf will be the focus of a special session at the Ocean Sciences Meeting in Honolulu in February, 2002. This work has led to the collaboration of Robert Chen with Chuck Hopkinson and Peter Raymond from the Marine Biological Laboratory working in the Plum Island Ecosystems LTER. The Mini-Shuttle, developed for this project, is being scheduled for possible work on natural oil seeps (Santa Barbara Channel), Appalachicola Bay NERRS (with Florida A & M University, an HBCU), and episodic, thin layer transport of nutrients (Boston Harbor).

RELATED PROJECTS

1.) Juanita Urban-Rich is examining the role of zooplankton in controlling CDOM distributions in coastal waters. Ship-time and equipment as well as results are being shared.

2.) Dan Repeta and I are studying the production of CDOM by phytoplankton in culture.

3.) Mary-Ann Moran (U. Georgia), Richard Zepp (EPA), Mark Wells (U. Maine), Paula Coble (U. South Florida), Juanita Urban-Rich (UMassBoston), Paul Bisset (Florida Environmental Inst.), Gary Hitchcock (U. Miami), Rod Zika (U. Miami), and Catherine Clark (Chapman U.) all participated in some way (on cruise or obtained samples) from our Gulf of Mexico cruises. These projects will all therefore be related.

PUBLICATIONS

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